STUDIES ON SUPERCONDUCTOR/NANO COMPOSITE OF BSCCO/$BiFeO_3$

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

Master of Science in Physics

By

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CERTIFICATE

*THIS IS TO CERTIFY THAT THE THESIS ENTITLED "**STUDIES ON SUPERCONDUCTOR/NANO COMPOSITE OF BSCCO/$BiFeO_3$**" SUBMITTED BY Mr. SUVASIS SWAIN IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE DEGREE IN PHYSICS AT NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA, IS AN AUTHENTICATE WORK CARRIED OUT BY HIM UNDER MY SUPERVISION AND GUIDANCE.*

TO THE BEST OF MY KNOWLEDGE, THE MATTER EMBODIED IN THE THESIS HAS NOT SUBMITTED TO ANY ORGANISATION.

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May 11, 2011 *Suvasis Swain*

Contents

Abstract

Superconductor BSCCO and BFO composite sample is prepared by sol-gel combustion technique using glycine as the fuel. X-ray diffraction results confirm the formation of BSCCO as major phase with some moderate amount of impurity phases. The SEM images of the sintered BSCCO and BFO composite pellet show that the samples so prepared are having distribution of grain sizes. EDXS of sample shows that the elemental composition is free from any foreign elements contamination. R-T measurement is done for all the samples. The T_C for BSCCO is coming out to be around 60 K. The BFO added BSCCO samples show semiconducting behaviour as high concentration of magnetic impurity decouples the cooper pairs.

CHAPTER 1:

A BRIEF HISTORY OF SUPERCONDUCTIVITY:

The discovery of superconductivity brings a tremendous change in the field of Science and Engineering from twentieth century onwards. The zero resistivity (or infinite conductivity) of a metal is known as superconductivity and this property of metal can be observed only at very low temperatures. Research is being carried out to develop superconductors for high temperatures. If it is made possible, superconductors will bring

- New revolutions in the field of miniaturization.
- The traditional wheel will largely disappear with the introduction of magnetic levitation trains and vehicles.
- The use of superconducting cables will almost eliminate electrical transmission losses.
- The heat generation in microelectronic circuits will be almost eliminated and more powerful computers will come into existence. Finally development of superconductors may take the present world in to new dimensions.

1.1 INTRODUCTION:

The discovery of superconductivity started from the findings of the Dutch physicist **Heike Kammerlingh Onnes** in 1911 that the resistance of mercury has an abrupt drop at a temperature of 4.1 K and has practically a zero dc resistance value at temperature below 4.1K.This new phenomenon of zero resistance at low temperatures was soon found in many other metals and alloys. The temperature at which superconductivity first occurs in a material is termed as critical or transition temperature (Tc).

A new era in the study of superconductivity began in 1986 with the discovery of high critical temperature superconductors. This discovery has opened a new subject matter called the "**High temperature superconductivity".** Efforts are also being made to develop "Organic Superconducting materials".

1.2 PROPERTIES OF SUPERCONDUCTORS:

- CRITICAL FIELD: In superconductors, their normal resistance may be restored if a magnetic field greater than the critical value H_c is applied to the specimen. H_c depends both on the material and on the temperature (T). It tends to H_0 as T tends to 0^0 K. In general for higher value of H_c the T_c value is lower and vice versa.

- CRITIICAL CURRENT DENSITY: An electric current is always associated with a magnetic field. Hence if a superconductor carries a current such that the field which it produces is equal to Hc, then the resistance of the sample will be restored. The current density at which it occurs is called the critical current density.
- MEISSNER EFFECT OR DIAMAGNETISM: The expulsion of magnetic flux by the superconductors when they are placed in the magnetic field is known as Meissner's Effect. From the Meissner's effect the magnetic flux inside the superconducting specimen is zero but from the magnetic materials we know that

  $$\mathbf{B = \mu_0 (H+M)}$$
  $$\mathbf{\Rightarrow 0 = \mu_0 (H+M)}$$
  $$\mathbf{\Rightarrow H = -M \text{ (or) } \chi = -1}$$

  Where χ is susceptibility of the material.

  From the above relation it can be said that the applied magnetic field get into utilize to magnetize the substance in an opposite direction. This is clearly, a diamagnetic behaviour of the superconducting materials and its susceptibility.
- FLUX QUANTIZATION: London, in 1950, speculated that the magnetic flux passing through a superconducting ring or a hollow superconducting cylinder can have values equal to nh/e, where n is an integer. This flux quantization in the non-superconducting region is simply the consequence of the fact that the non-superconducting region is surrounded by the superconducting region. The flux quantization has been confirmed experimentally but the quantum of flux has been found to be h/2e rather than h/e. This unit of flux is called a fluxoid.
- JOSEPHSON EFFECT: Josephson observed some remarkable effects associated with the tunnelling of superconducting electrons through a very thin insulator (1-5 nm) sandwiched between two superconductors. Such an insulating layers forms a weak link between the superconductors which is referred to as the Josephson junction. (i)The dc Josephson effect: A dc current flows across the junction even when no voltage is applied across it. (ii)The ac Josephson effect: An application of rf voltage along with the dc voltage can result in the flow of direct current through the junction. Hence this effect has been utilized to measure e/h very precisely and may be used as a means of establishing a voltage standard.
- TYPES OF SUPERCONDUCTORS: Superconductors have been classified as type I

and type II depending upon their behaviour in an magnetic field, i.e., how strictly they follw the Meissner effect. (i) Type I (soft) superconductors: The superconductors which strictly follow the Meissner effect are called type I superconductors. These superconductors exhibit perfect diamagnetism below a critical field H_c. As the applied magnetic field is increased beyond H_c, the field penetrates the material completely and the latter abruptly reverts to its normal resistive state. These materials give away their superconductivity at lower field strength and are reffered to as the soft superconductors. (ii) Type II (hard) superconductors: These superconductors donot follow the Meissner effect strictly, i.e. the magnetic field does not penetrate these materials abruptly at the critical field. For field less than H_{c1}, the material axist in the superconducting state. As the field exceeds H_{c1}, the flux begins to penetrate the specimen and, for $H=H_{c2}$, the complete penetration occurs and the material becomes a normal conductor. The field H_{c1} and H_{c2} are called the lower and upper critical fields respectively. In the region between the fields H_{c1} and H_{c2} the diamagnetic behaviour of the material vanishes gradually and the flux density B inside the specimen remains non-zero, i.e., the Meissner effect is not strictly followed. The specimen in this region is said to be existing in the vortex or intermediate state.

- BCS THEORY: The understanding of superconductivity was advanced in 1957 by three American physicist- John Bardeen, Leon Cooper and John Schrieffer , through their Theories of Superconductivity, known as the BCS Theory. The BCS Theory explains superconductivity at temperature close to absolute zero. The fundamental idea underlying BCS theory is that electrons pair up with one another due to a special type of attraction (interaction). These pairs of electrons are called copper pairs. Normally two electrons repel each other. However, the electrons could attract each other via distortion of the lattice. The idea is if we consider an electron passing close to an ion, there will be a momentary attraction between them which might slightly modify the vibrations of the ion. This in turn could interact with a second electron nearby which will also be attracted to the ion. But net effect of these two interactions is that there is an apparent attractive force between the two electrons and this would not have arisen if the ion had not been present. The BCS theory is able to explain all the properties shown by the superconductor.

1.3 **HIGH T_c SUPERCONDUCTOR**:

In the year 1986 for the first time, superconductivity was observed in oxides ($La_{2-x}Ba_xCaO_4$) with T_c as high as 30 K. Soon after this many other oxide based superconductors

were discovered and much importantly there T_c and J_c was much higher than alloys like NbTi and Nb_3Sn. This opened a new branch of high T_c superconductivity namely "High T_c superconductivity" as they broke the barrier of 30K imposed by BCS theory.

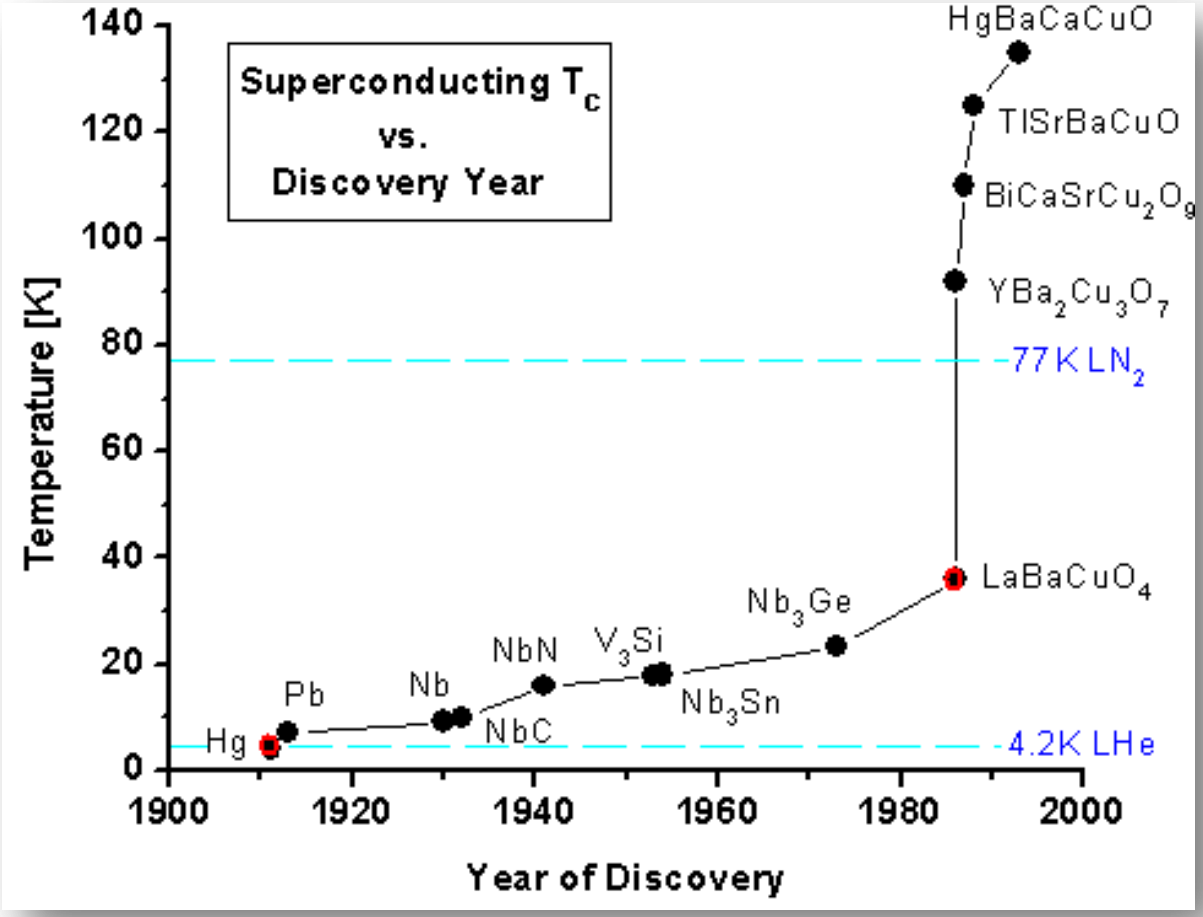


Fig 1: History of superconductivity

They have their structure derived from ideal perovskite structure (therefore termed as defect perovskite structure), either through an intergrowth phenomenon or by an ordered removal of oxygen atoms. They have a layered crystal structure consisting of one or more CuO_2 layers. Copper is present in the mixed state involving a partial oxidation of Cu^{2+} to Cu^{3+}. There is a charge transfer, to and from the CuO_2 layers, which is induced by doping near the metal insulator phase existing in all oxide high T^c superconductor.

- LBCO: LBCO is the first oxide based HTSC material having T_c equal to 35 K. It is the only insulating material in the HTSC family. This discovery stimulated a great deal of additional research in high T_c superconductivity on cuprate materials with

structure similar to LBCO.

- YBCO: YBCO is the first material to break the liquid nitrogen temperature. The highest Tc achieved by YBCO system is around 90 K. YBCO system is highly studied as it is the most cleanest and most ordered crystals.
- BSCCO: BSCCO is the next higher member of HTSC family. General formula of BSCCO system is $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$ withspecific transition temperature ranging from Tc=20 K(n=1, 2201 phase), 85 K (n=2, 2212 phase) and 110 K (n=3, 2223 phase). The only difference between two consecutive phases is the addition of a double Ca-Cu-O_2 in the unit cell.
- TBCCO: TBCCO is the next higher member of HTSC family. General formula of TSCCO system is $Ti_2Ba_2Ca_{n-1}Cu_nO_{2n+4+x}$ withspecific transition temperature ranging from Tc=85 K(n=1, 2201 phase), 110K (n=2, 2212 phase) and 125 K (n=3, 2223 phase). The CuO_2 layers are thicker and closer together in comparison to BSCCO system.
- HBCCO: HBCCO is the highest member of HTSC family till today. General formula of HBCCO system is $Hg_1Ba_2Ca_{n-1}Cu_nO_{2n+2+x}$ withspecific transition temperature ranging from T_c=94 K (n=1, 1201 phase), 128 K (n=2, 1212 phase) and 134 K (n=3, 1223 phase).The Tc of the Hg compound containing one CuO_2 layer is much larger as compared to the one CuO_2 layer compound of TBCCO.

1.4 **WHY BSCCO**:

- ✓ A Bi-based superconductor is having higher Tc and shows more stability in superconucting nature w.r.t. oxygen loss in comparision to YBCO.
- ✓ In Bi-based cuprates there is no rare earth element.
- ✓ STM and ARPES are suitable in BSCCO system.
- ✓ As anisotropy is more than other cuprates, it is facinating to study the properties.

1.5 CRYSTAL STRUCTURE OF BSCCO:

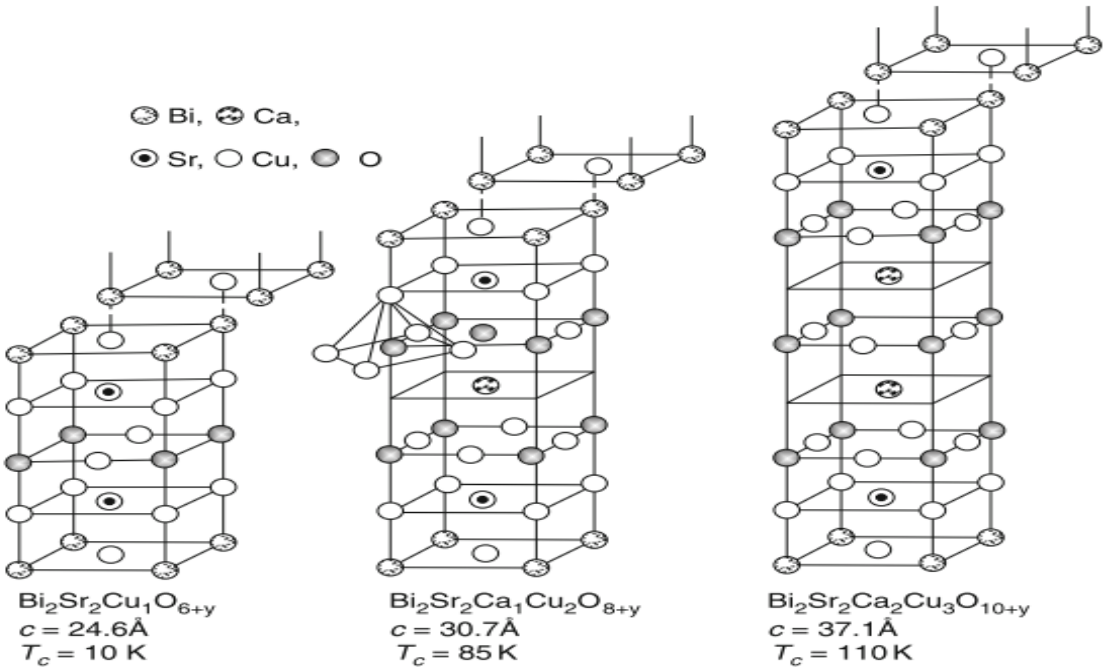


Fig 2: Crystal structure of BSCCO family

1.6 MOTIVATION:

Superconductors are diamagnetic, hence completely repels magnetic lines of force until magnetic field Hc_1. If the magnetic field is increased further, the magnetic flux starts penetrating into the superconductor in the form of vertices. With further increase in field strength more number of magnetic fields penetrates into it until Hc_2, beyond which all lines of force penetrates, i.e. normal region.

When a magnetic field penetrates into the superconducting region, it creates an electric field. In the presence of both electric and magnetic field, vortices experience Lorentz force i.e. (J*B)/C, where J represents critical current density, B is the magnetic field and C is an arbitrary constant. So vertices start to flow in mixed state region. When flux lines flows, it experiences a viscous drag force F_v which opposes this motion i.e. ηV_L inside the medium, where V_L-vortex velocity and η-proportionality constant. The driving force is balanced by viscous force per unit length of vortex line. In the absence of pinning

$(J*B)/C = \eta V_L$

i.e. $F_L = (J*B)/C - \eta V_L = 0$

When the Lorentz force (F_L) overcomes the viscous force (F_V) at higher magnetic field field, the vortex or flux line starts moving. As the vortices move, critical current density (J_C) decreases. For a practical application point of view we have to stop the vortex movement, thereby enhancement of J_C. The microscopic impurities and defects in the superconductor have been found to be acting like pinning centre for the flux motion. When pinning force (F_p) is greater than Lorentz force (F_L), it pins the vortex motion.

High temperature superconductors (HTSC) of granular shapes have grain boundary. Superconductivity originates inside the grain boundary acts like pinning centres and prevents vortex motion. By addition of suitable microscopic impurity to the HTSC, impurity makes a weak link between two superconducting grains by forming a Josephson junction. So that cooper pair can easily tunnel through the impurity.

So composites of nano particles of metal, insulator and oxides are very interesting in HTSC. Metal/HTSC composite concern essentially Ag, Snand Au metals. Bi-2223/Ag composite have large critical current and large application field in composite tapes. Oxides like SnO_2 In_2O_3, $Bi_2Sr_3CaO_7$ and Bi2CuO4 are also studied by various researchers. From the literatue, it is concluded that out of all, magnetic nano inclusion are more suitable to enhance J_C. As $BiFeO_3$ (BFO) having superparamagnetic behaviour and also a Bi based perovskite structure may act as effective artificial pinning centre.

1.7 LITERATURE SURVEY:

I.**A.Ghattas et.al.,Al-based nano particles in (Bi,Pb)-2223, Physica C: Superconductivity, 468, 31 (2008)**

The effect of nano-size Al_2O_3 (40 nm) addition on the microstructure and pinning properties of polycrystalline (Bi, Pb) - 2223 was analyzed. The Al_2O_3 content in the sample varied from 0.0 to 1.0 wt.% of the total mass of the sample. Upto 0.2 wt.% J_C and T_C value has been increased.

II. **M.Zouaoui *et al., N*ano-size ZrO_2 (Bi, Pb)-2223, *Supercond. Sci. Technol.* 21, 125005 (2008)**

The effect of nano-size ZrO_2 (10-20nm) addition on the microstructure and pinning properties of polycrystalline (Bi, Pb) -2223 was analyzed. The ZrO_2 content in the sample varied from 0.0 to 0.3 wt.% of the total mass of the sample. Upto 0.1 wt.% J_C and T_C value has been increased.

III. **N. A. Hamid et .al., TiO_2 nanoparticles in BSCCO, J. Mater. Sci. 35, 2325(2000)**

The effect of nano-size TiO_2 addition on the microstructure and pinning properties of polycrystalline (Bi, Pb) -2223 was analyzed. The TiO_2 content in the sample varied from 0.05 to 0.1 wt.% of the total mass of the sample. The J_C, T_C and C-axis parameter decreases with the addition of TiO_2.

IV. **B.A. Blbiss et. al., magnetic nanoparticles in bscco , Solid state communications 150, 1542 (2010)**

The effect of nano-size NiO addition on the microstructure and pinning properties of polycrystalline (Bi, Pb) -2223 was analyzed. The NiO content in the sample varied from 0.001 to 0.005 wt.% of the total mass of the sample. The J_C and T_C increases with the addition of NiO. In this paper it is inferred that Magnetic nanoparticles may act as pinning sites in granular superconductors in applied magnetic field.

1.8 APPLICATION:

1.8.1. APPLICATION OF JOSEPHSON'S EFFECT

- ✓ Superconducting quantum interface device (SQUIDS): SQUIDS can be used for the measurement of small magnetic field and their small changes. From M-H loop the critical current density can be measured.
- ✓ Magnetic Resonance Imaging (MRI): MRI of human skull.

1.8.2 ELECTRICAL APPLICATION:

- ✓ ELECTRICAL GENERATORS: Electrical generators made with superconducting wire are more efficient (efficiency above 99%) than conventional generator wound with copper wire.
- ✓ POWER TRANSMISSION: Persistent current should make the superconductors more preferable than normal cables.
- ✓ SUPERCONUCTING MICRO CHIP: This will lead to smaller and much more powerful supercomputers.
- ✓ SATELITE COMMUNICATION: Among emerging technology is a stabilizing for earth orbiting satellites that employs the properties of imperfect superconductors to reduce friction to near zero.

- ✓ INTERNET COMMUNICATION: Internet data traffic is doubling every 100 days, superconductors' technology is being called upon to meet this super need.

1.8.3 MAGNETIC APPLICATION:

- ✓ MAGNETIC LEVIATION: The superconductor repels the majority of the magnetic force lines, which support and leviate the magnet.
- ✓ STORING ELECTRICAL POWER: Once the current is induced in the superconducting materials its lack of resistance allows the induced current to flow forever. These permanent current in a superconductor also produce a magnetic field around the superconductor, creating a powewrful electromagnet.

1.8.4 MEDICAL APPLICATION:

- ✓ Superconducting devices like, SQUIDS, Superconductors are also employed in magnetic resonance imaging (MRI) diagnostic techniques which rare widely used in these days.

CHAPTER 2:

EXPERIMENTAL:

Synthesis of BSCCO system is the most important of my research work due to its anisotropic nature and large c-axis parameter. Different kinds of methods have been adopted for the preparation of BSCCO system.

2.1 LITERATURE SURVEY FOR BSCCO SYNTHESIS:

I. **J.Bock .et.al.,Solid state communication Vol.72,453-458 (1989):**

Sample is prepared by melt process method with starting material Bi_2O_3, SrO, CaO and CuO mixed together and heated in a aluminium crucible upto 1000-1100 ^{0}c and cooled in a controlled manner. T_c was found to be 85 K.

II. **M.O.Petropoulou.et.al.,Journal of thermal analysis,Vol 52,903-914, (1998)**

Sample is prepared by solid state reaction route with a comparison between one step and two step method. In single step method, the starting materials are Bi_2O_3, $SrCo_3$, $CaCo_3$ and CuO were mixed in the molar ratio and calcined at 830-845 ^{0}C . In two step process $SrCo_3$, $CaCo_3$ and CuO were mixed in the molar ratio and mixture was heated at 955^{0}C. Then Bi2O3 added and heated at 845 ^{0}C. Impurity phase of 2201 was found. T_c was found to be 77 K and 85 K respectively.

III. **A.Tampieri et,al.,Physica C 34,157-161, (1993)**

Sample is prepared by solid state synthesis route using high purity commercial powders Bi, Cu, Pb, Sr and Ca were wet-mixed in alcohol in strochiometric ratio in nylon jars with polythelene balls then calcination and sintering were taking place at 780 ^{0}C and 850 ^{0}C.

IV. **Hanjin Lim.et.al.,Journal of materials science,Vol 31,2349-2352, (1996)**

Sample is prepared by solid state route with starting material Bi_2O_3, $SrCo_3$, $CaCo_3$ and CuO powders were combined with strochiometric ratio and then powders were ballmilled with isopropanol and ZrO_2 grinding media.Impurities phases of CaO, CuO & Ca_2CuO_3 & minor peak of 2223 exist.

V. **A.Tampieri et,al.,Physica C 306,21-33,(1998)**

Sample was prepared by three different method i.e. solid state, pyrolysis and sol-gel reaction. Single phase was found in the sol-gel method. All metallic oxides were taken as the starting

materials. Cao, CuO and BSCCO 2201 impurity phase were found in solid state and pyrolysis method but almost single phase was obtained in sol-gel method.

VI. **M.Arshad .et.al.,Journal of thermal analysis and calorimetry,Vol. 89,595-600 (2007)**

Sample was prepared by sol-gel method with starting material as all metallic nitrate and EDTA as the chelating agent. Few drops of NH_4OH was added to adjust PH value of the solution. The precursor powder was heated at 800 ^{0}C and sintered at 845 ^{0}C and 860 ^{0}C correspondingly.

2.2 INFERENCE FOR BSCCO SYNTHESIS:

From the above mentioned literature it is observed that there are several methods of preparation for BSCCO, i.e. solid state synthesis route, melt process, pyrolysis and sol-gel synthesis route. Out of all synthesis route sol-gel route gives nearly the single phase. In liquid phase technique the constituents are mixed in the atomic level and then the lattice growth occurs. But in solid state the powder is obtained by crossing the different planes in the lattice. Another advantage of Liquid phase combustion synthesis is that the chances of impurity are lesser than the solid state synthesis. The advantages of sol-gel method over all other synthesis root are (i) It gives better homogeneity, (ii) yields less particle size and (iii) require shorter heat treatment. So the liquid phase combustion synthesis is chosen for the preparation of the sample.

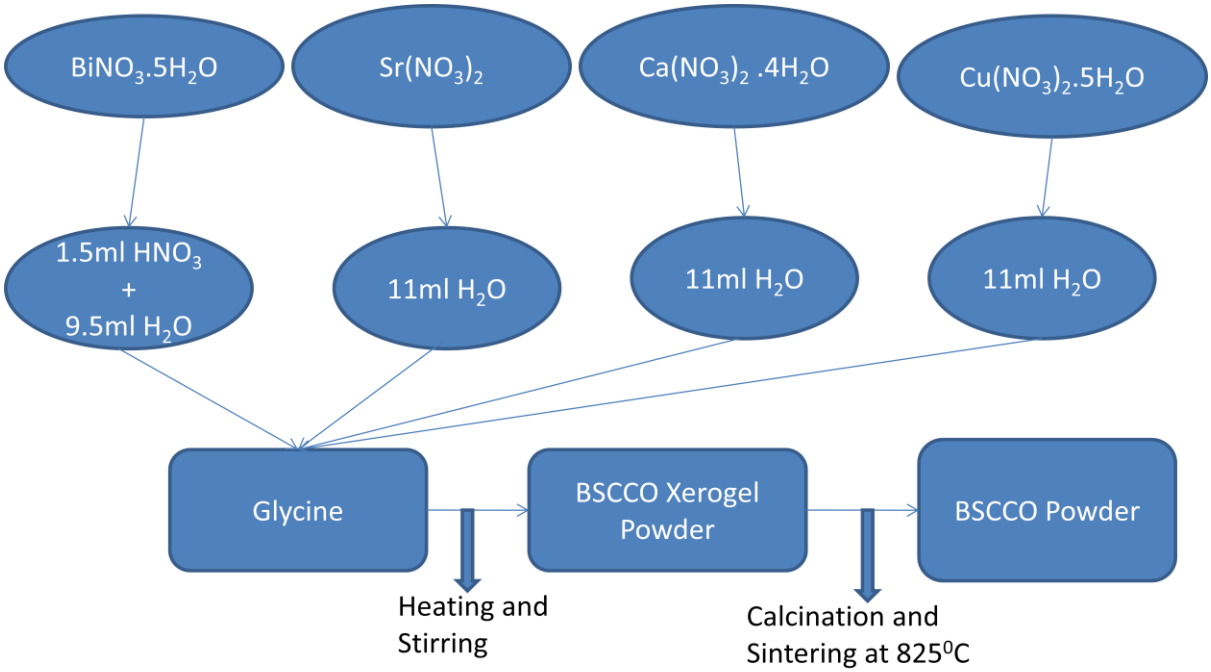
2.3 SYNTHESIS OF BSCCO:

The samples are prepared by sol-gel combustion route. Glycine is chosen as the fuel for the synthesis. It is reported that, solvent with PH: 5-6 has to be maintained for the preparation of sample. All metallic nitrates, i.e. $Bi(NO_3)_2.5H_2O$, $SrNO_3$, $Ca(NO_3)_2.4H_2O$, $Cu(NO_3)_2.3H_20$ (MERK) are taken in strochiometric ratio and dissolved in distilled water (MARS). But $Bi(NO_3)_2.5H_2O$ is not dissolved in water so we first dissolve it with Nitric acid (1.5ml) and then with water. 10% Bi excess is added to compensate for eventual bismuth loss during thermal treatment. All the solutions are added to the chelating agent (glycine). The color of the solution is found to be light sky color. A continuous slow heating and stirring is maintained throughout the experiment. Initially precipitation is taking place due to the low PH value. After 4-5 hours gel is formed without any precipitation due to the evaporation of water from the solution as the PH value 5-6 is maintained during geletion. Here the light sky color changes to deep sky color. After 30 minute precursor powder is obtained with vigorous

reaction whose color is turned black. The powder collected is then calcined for 5 hours at a temperature 800 ^{0}C. The furnace heating rate is maintained as 5 ^{0}/minute. After cooling to room temperature, the sample is collected from the furnace and is then grinded by agate mortar. The sample is then pressed into pellet by dry pressing method and the pellet is then sintered upto 825 ^{0}C with intermediate crushing and grinding for 25 hours for each 5 ^{0}C rise in temperature. The grinded power is now ready for necessary characterization.

2.4 FLOW CHART FOR BSCCO SYNTHESIS:

PROCEDURE



2.5 LITERATURE SURVEY FOR BFO SYNTHESIS:

I. **Carvalo et al., Material letters. 62, 3984 (2008)**

Sample is prepared by sol-gel combustion method with starting materials Bi_2O_3(99.9%) and Fe_2O_3 (99.95) dissolved in dilute nitric acid. Urea was used as fuel in molar ratio [urea]/{[Bi]+[Fe]} of 3. After ignition, brown powder was obtained. The powder was pressed into disc and then treated 500 ^{0}C and atmosphere.

II. Hardy et al. Journal of European Ceramic society. 29, 3007 (2009):

Starting products for synthesis are Bi(III) citrate, Fe(III) citrate hydrate, Fe(III) nitrate non hydrate and citric acid. The concentration of metal ions to citric acid is equal to 1:1. 10% Bi excess is added to compensate for eventual bismuth loss during thermal treatment.

III. Xue et al., Materials Research Bullet. 43, 3368 (2008):

BFO powder was synthesized by a solution evaporation process. 0.1 mole of $Bi(NO_3)_2.5H_2O$ and 0.01 mole of $Fe(NO_3)_3.9H_2O$ were taken initially dissolved in the dilute nitric acid to form a transparent solution. EDTA in 1:1 mole ratio with respect to the metal nitrates was added to the above solution. The solution is then heated at 130^0C under constant stirring in oil bath until all liquids get evaporated out from the solution. The powder was then collected and sintered for 350s in air at different temperatures (300 ^{0}C - 600 ^{0}C) using rapid thermal processor with heating rate upto 80 ^{0}C/s to get $BiFeO_3$ nanoparticles.

2.6 INFERENCE OF BFO SYNTHESIS:

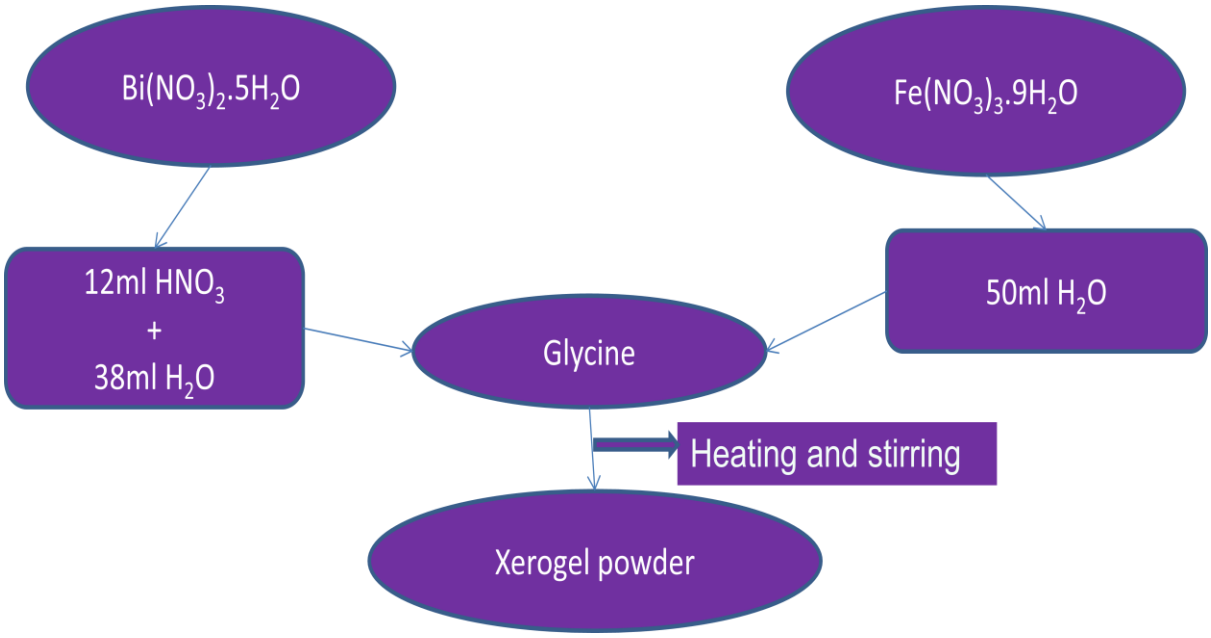
As the chemical synthesis route is the best and simplest route which gives better mixing and homogeneity with nano size particle, it is chosen for synthesis of BFO.

2.7 SYNTHESIS OF BFO:

The samples are prepared by sol-gel combustion route. Glycine is chosen as the fuel for the synthesis. It is reported that, solvent with PH: 1 has to be maintained for the preparation of sample. All metallic nitrates, i.e. $Bi(NO_3)_2.5H_2O$, $Fe(NO_3)_3.9H_2O$ (MERCK) are taken in strochiometric ratio. But $Bi(NO_3)_2.5H_2O$ is not dissolved in water so we first dissolve it with dilute Nitric acid. Ferric nitrate is dissolved in 50ml of distled water and Bismuth nitrate is added in the solution of 38ml water and 12ml nitric acid. All the solution is added to the glycine. A continuous slow heating and stirring is maintained throughout the experiment. The solution is now brick in color. After 2-3 hour precursor powder is formed after geletion with tremendous reaction and here the same color is found. Then the powder is finely grinded by agate mortar.

2.8 FLOW CHART FOR BFO SYNTHESIS:

PROCEDURE



2.9 SUPERCONDUCTOR/NANO COMPOSITE OF BSCCO/$BiFeO_3$:

To obtain nano composite of BSCCO/BFO we added BFO (5 wt %) to BSCCO. The sample is then pressed into pellet by dry pressing method and is then sintered at temperature of 800 ^{0}C. The pellet so formed is now ready for necessary characterization.

CHAPTER 3:

RESULTS AND DISCUSSION

I. XRD ANALYSIS:

Phase analysis was studied using the room temperature powder X-ray diffraction (Model: PW 1830 diffractometer, Philips, Netherland) with filtered 0.154 nm Cu Kα radiation. Samples are scanned in a continuous mode from 20^0 – 60^0 with a scanning rate of 2^0/minute. The samples so prepared are calcined for various temperature (800 ^{0}C – 850 ^{0}C) to optimize. At 850 ^{0}C the formation of 2223 phase starts which is confirmed from the XRD data. So finally we optimize our temperature to 825 ^{0}C. We varied the Sr:Ca ratio from 1.5:1.5 to 2:1.5. The best result obtained from the sample having Sr:Ca ratio 1.8:1.5. Here is a comparison between the samples having Sr:Ca ratio 2:1.5 and 1.8:1.5. During sintering process, the samples having Sr:Ca ratio 1.5:1.5 completely melts out. So finally we take the above two ratios (fig.3 and fig.5) for all characterization. XRD Plot of 5 wt % BFO added BSCCO (2 2 1.5 2 and 2 1.8 1.5 2) are given in figure 4 and 6 respectively. The major peaks correspond to the 2212 phase. Besides these prominent peaks, some other peaks of low intensity are also observed, which do not belong to other phases of BSCCO.

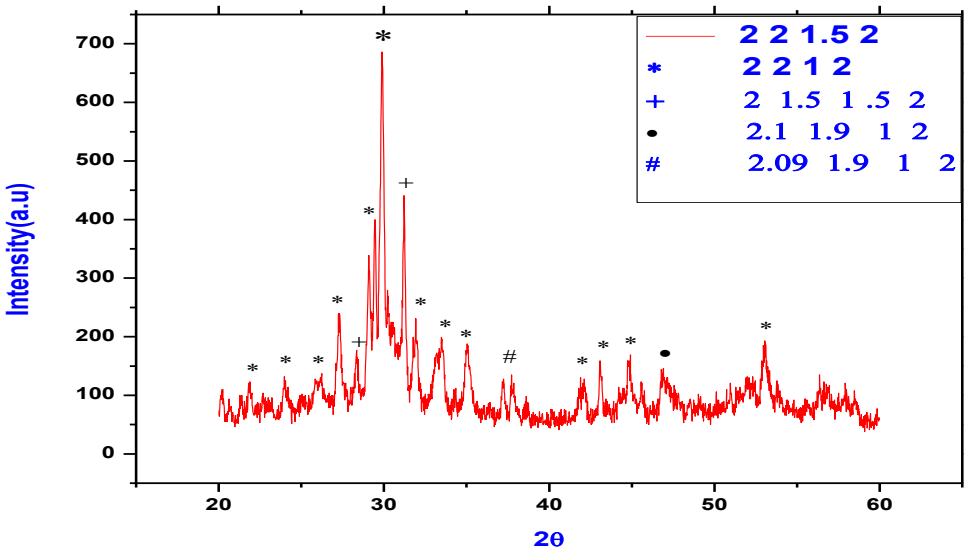


Fig.3: XRD plot for BSCCO 2 2 1.5 2

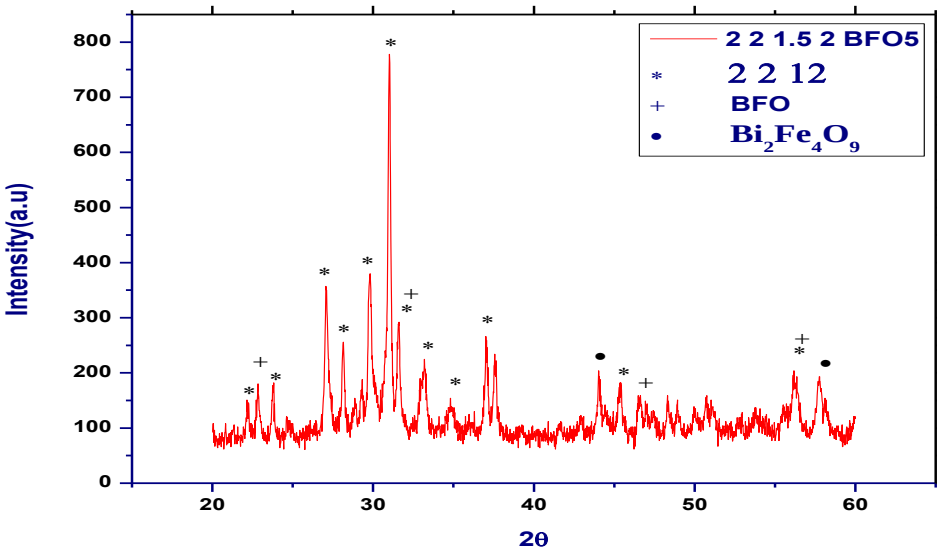


Fig.4: XRD plot for BSCCO 2 2 1.5 2 with 5 wt.% BFO

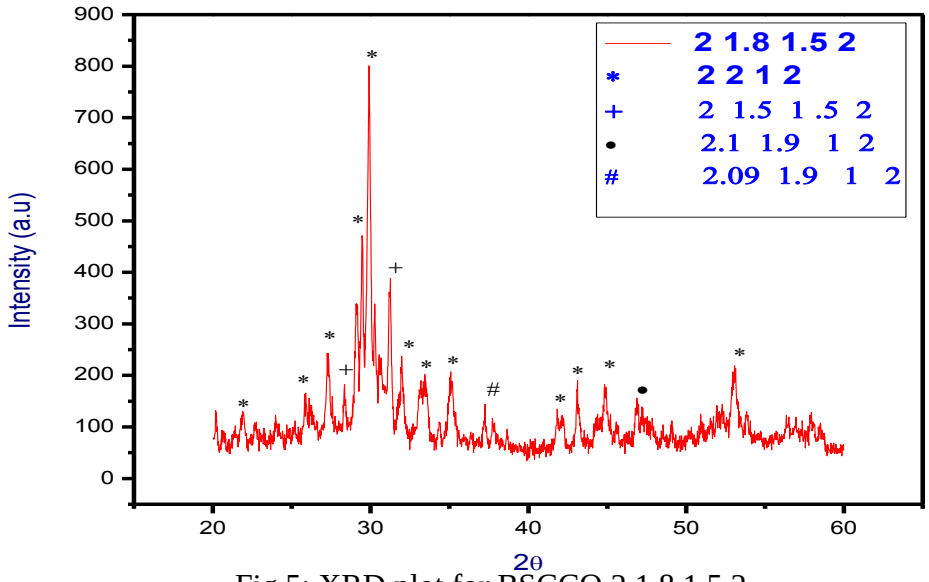


Fig.5: XRD plot for BSCCO 2 1.8 1.5 2

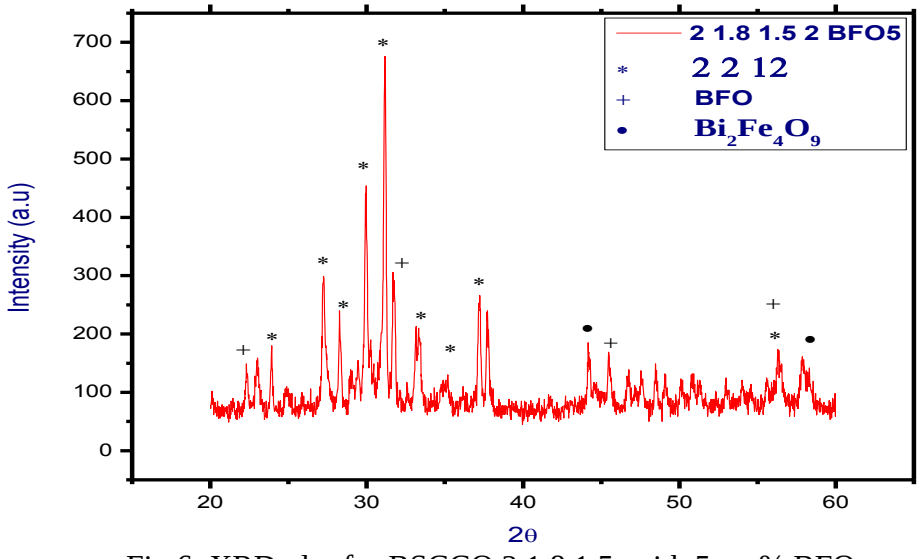


Fig.6: XRD plot for BSCCO 2 1.8 1.5 with 5 wt.% BFO

II. SEM ANALYSIS:

Microstructural features were studied using Scanning Electron Microscope (JSM 6480LV JEOL, Japan). The SEM microstructure of all samples (5 wt % of BFO added to BSCCO 2 2 1.5 2 and 2 1.8 1.5 2) is given below in figures 7, 8, 9, and 10. Figure 7 and 9 having magnification 850 and that of figure 8 and 10 are having 5000 magnification. It confirms the formation of BSCCO along with BFO. The dark region corresponds to BSCCO and the comparatively light region corresponds to BFO. In 5000 magnification, the rod like structure corresponds to BSCCO and the nearly rounded like structure represents BFO. It also indicates that BSCCO 2 2 1.5 2 having high concentration of BFO in comparison to BSCCO 2 1.8 1.5 2, which is confirmed from the R-T measurement.

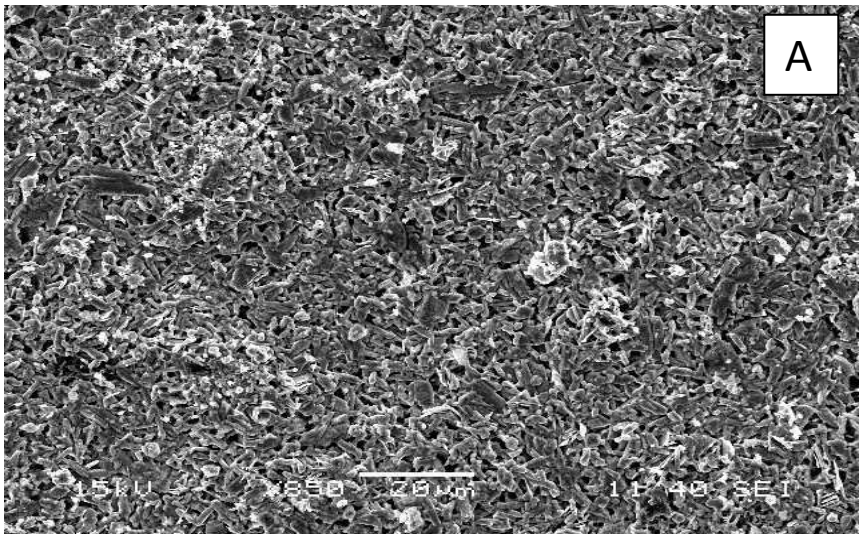


Fig.7: SEM of BSCCO 2 2 1.5 2 with 5 wt.% BFO (850 magnification)

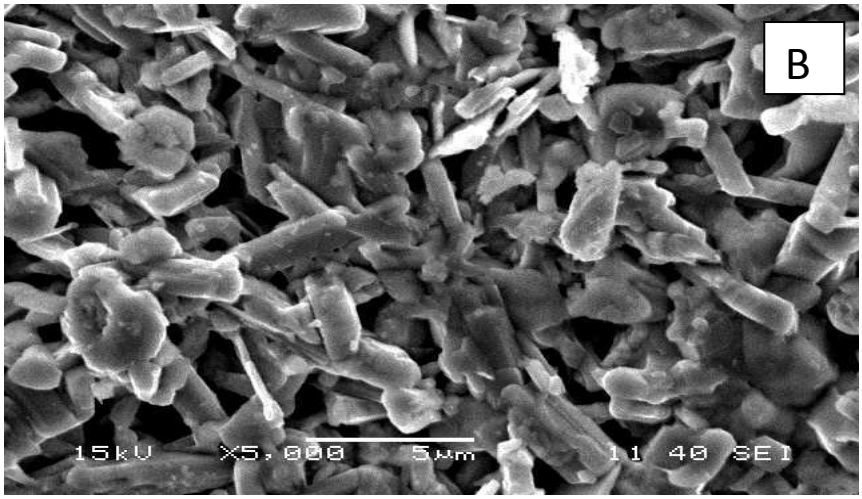


Fig.8: SEM of BSCCO 2 2 1.5 2 with 5 wt. % BFO (5000 magnification)

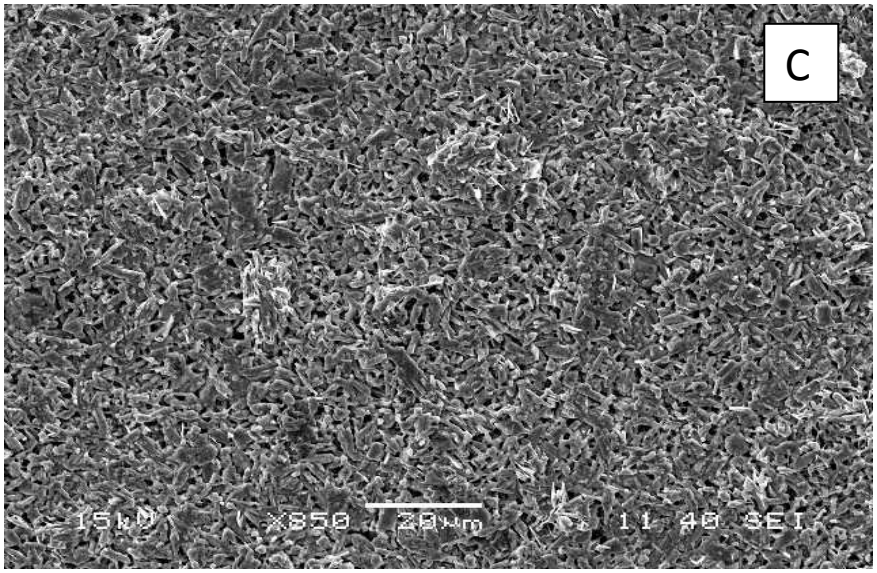


Fig.9: SEM of BSCCO 2 1.8 1.5 2 with 5 wt. % BFO (850 magnification)

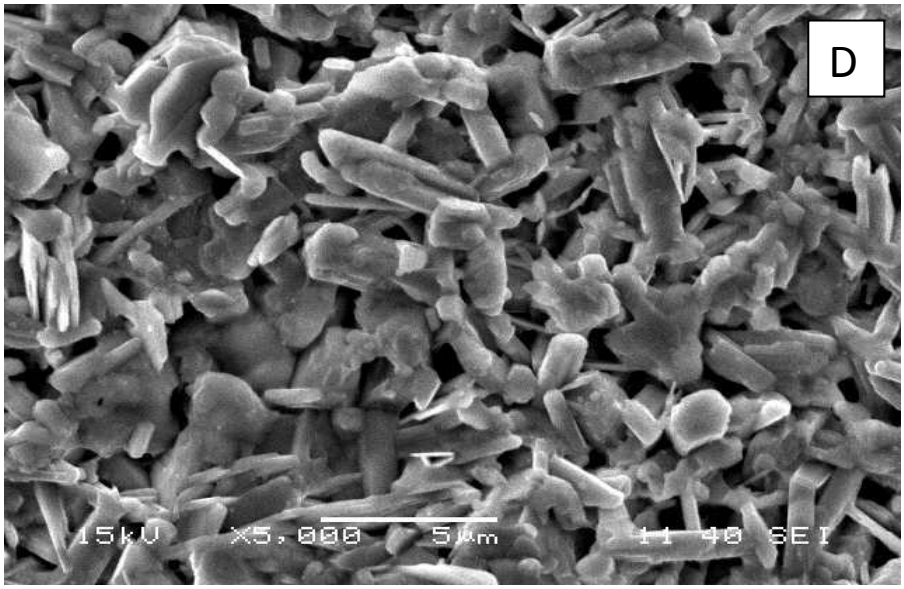


Fig.10: SEM of BSCCO 2 1.8 1.5 2 with 5 wt.% BFO (5000 magnification)

III. EDXS ANALYSIS:

The energy Dispersive X-ray spectrometer (EDXS) analysis of two samples (5 wt % of BFO added 2 2 1.5 2 and 2 1.8 1.5 2) is shown in the following figures (Fig.11 and 12). The EDXS plot reveals no extra peaks related to elements other than the constituents. All the samples show the exact match for standard peak position for Bi, Sr, Ca, Cu, Fe and Oxygen. This reveals that the elemental composition of all the samples does not contain any foreign elements.

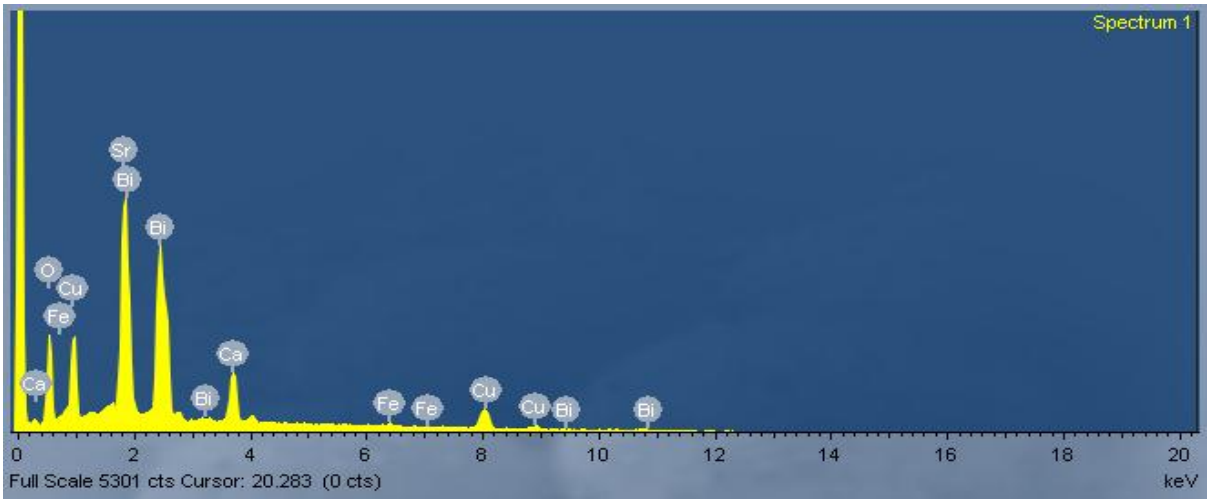


Fig.11: EDXS of BSCCO 2 2 1.5 2 with 5 wt.% BFO

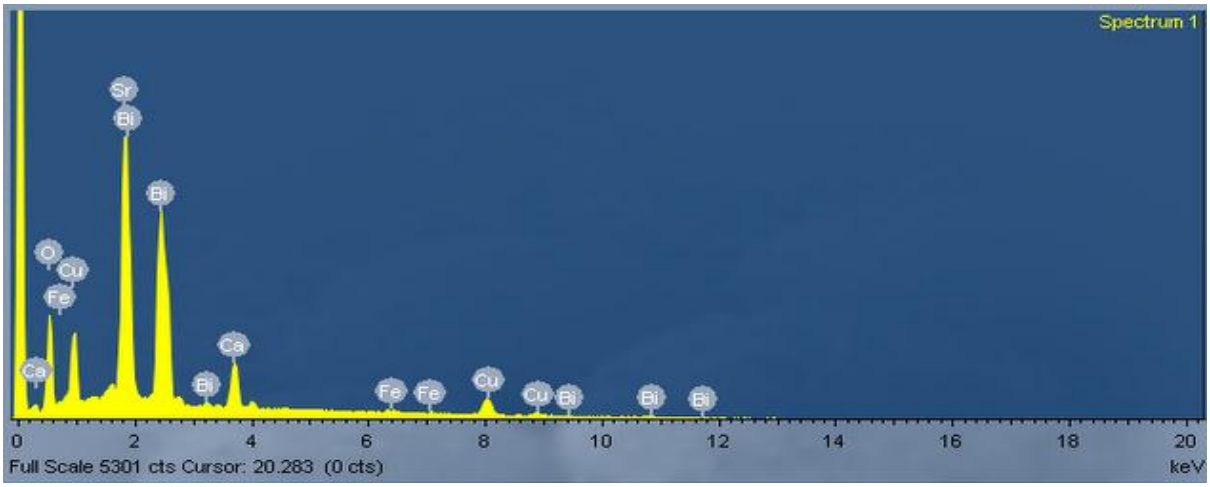


Fig.12: SEM of BSCCO 2 1.8 1.5 2 with 5 wt.% BFO

IV. R-T ANALYSIS:

R-T measurements of all samples is carried out using 4 probe arrangement. The temperature dependent resistance ρ (T) was measured using standard four-probe technique with a nanovoltmeter (Keithley-2182 A), Current source (Keithley 6221) and Temperature controller (Lakeshore 332). The plots are shown in the figure 13, 14 and 15. In both the unaided BFO samples, T_C is coming out to be around 60 K, which is low in comparison to the T_C value reported for BSCCO 2212 phase. It is due to the fact that some impurity phases are

forming along with the 2212 phase. When the measurements are taken for the 5 wt % of BFO added BSCCO, it is showing the semiconducting behaviour. It is here inferred that this is mainly due to the high concentration of BFO. It is also observed that the resistivity of added BSCCO 2 1.8 1.5 2 is less in comparison to BSCCO 2 2 1.5 2. It is due to the less percentage of BFO in BSCCO 2 1.8 1.5 2, which is confirmed from SEM.

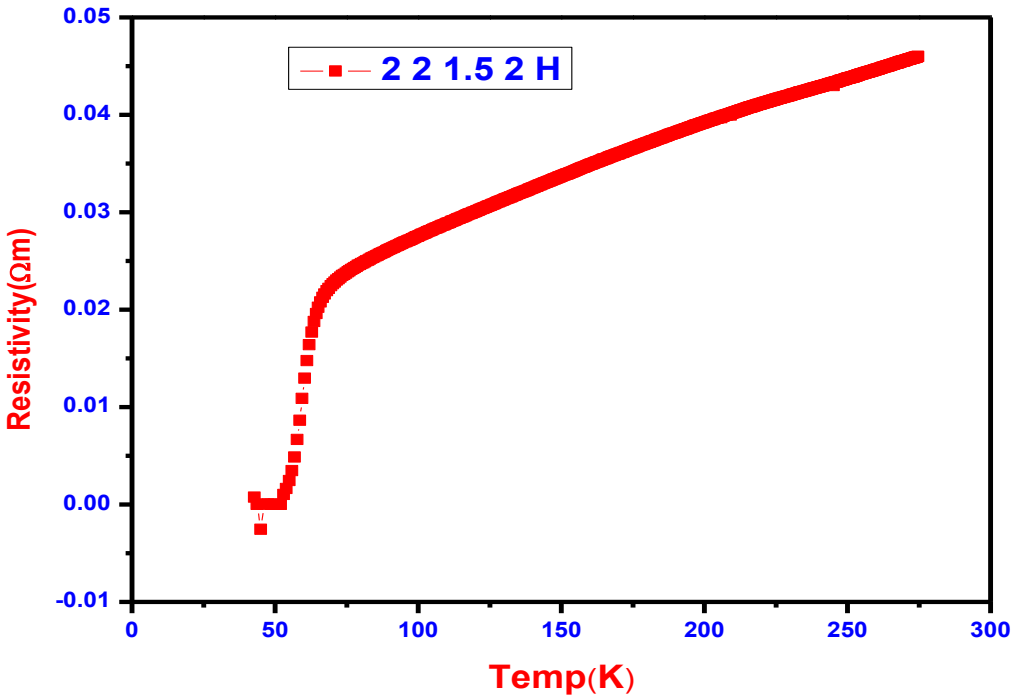


Fig.13: R-T plot of BSCCO 2 2 1.5 2

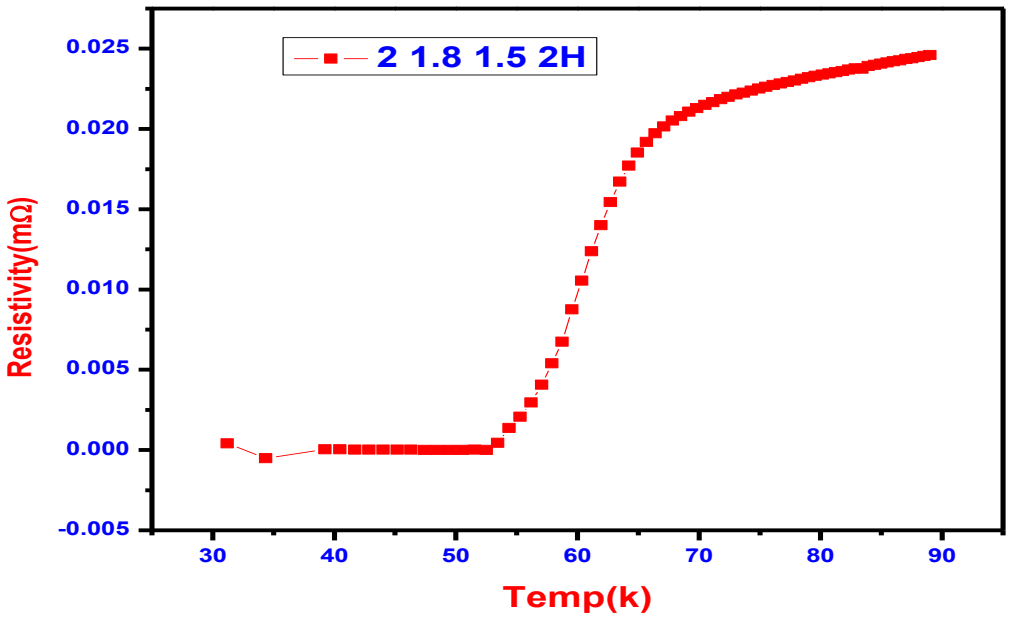


Fig.14: R-T plot of BSCCO 2 1.8 1.5 2

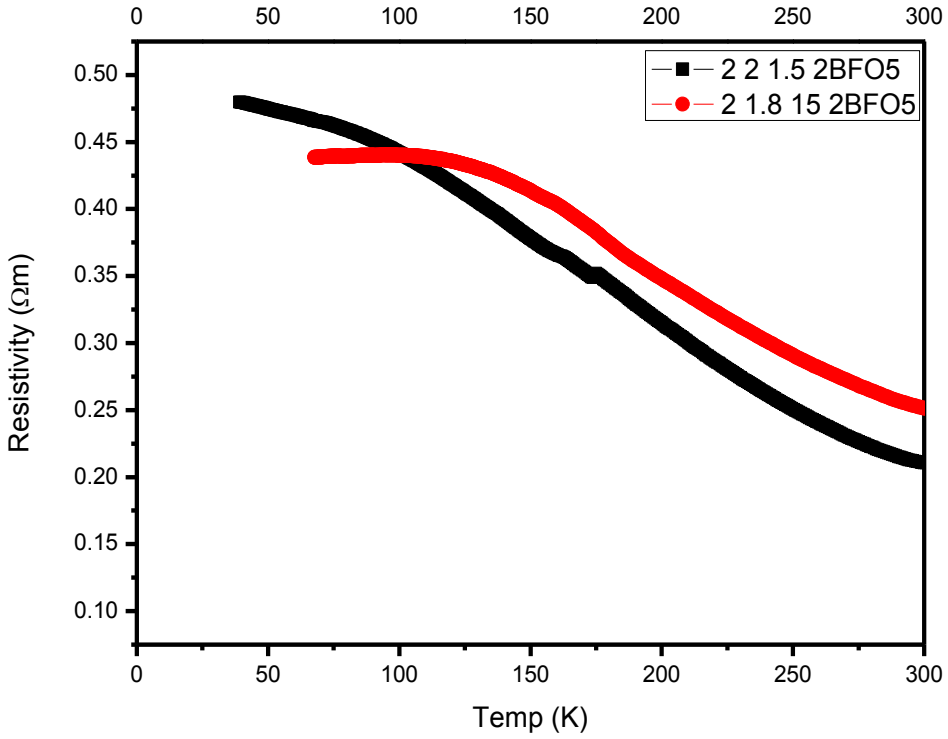


Fig.15: R-T plot of both the samples with 5 wt % of BFO

CHAPTER 4:

CONCLUSION:

The sample is successfully prepared by liquid phase combustion synthesis method. Depending upon the amount of melting we optimized our calcination temperature to 825 ^{0}C. After that we optimized the Sr:Ca ratio to 1.8:1.5. Moderate amount of impurity phases are observed which is confirmed by X-PERT High Score pattern analysis. The structure is confirmed to be orthorhombic with space group P_{222}. The lattice parameters are, a = 5.3918 A^0 , b = 5.4468 A^0 , c = 30.85 A^0. The particle size of BSCCO (2 1.8 1.5 2) is found to be 72 nm, which is calculated from Williamson Hall method. The impurity phases are indexed in the corresponding figures. In BFO added BSCCO the impurity phase ($Bi_2Fe_4O_9$) are coming only due to the Bismuth loss in higher temperature.

From SEM images of BFO added BSCCO, the presence of rounded shaped BFO is observed in rod shaped BSCCO. From SEM images, the conducting and non-conducting behaviour of BSCCO and BFO respectively, is confirmed from the color of the images.

The EDXS plot reveals no extra peaks related to elements other than the constituents. All the samples show the exact match for standard peak position for Bi, Sr, Ca, Cu, Fe and oxygen. This reveals that the elemental composition of all the samples does not contain any foreign elements and if any parasitic phases are there, it has to be some form of Bi, Sr, Ca, Cu, Fe and oxygen only.

R-T plot for BSCCO 2212 phase in both the cases (BSCCO 2 2 1.5 2 and 2 1.8 1.5 2) Tc is found to be around 60 K. After the addition of BFO, R-T curve shows the semiconducting behaviour. It is mainly due to the high concentration of BFO in BSCCO.

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